

The Green Line of Atomic Oxygen in the Day Airglow

JAMES C. G. WALKER

Institute for Space Studies, Goddard Space Flight Center, NASA, New York, N. Y.

(Original manuscript received 9 February 1965, in revised form 5 March 1965)

ABSTRACT

Important contributions to the $\lambda 5577$ dayglow may be made by dissociative recombination of O_2^+ and by photodissociation of O_2 . Both contributions are evaluated for a range of models corresponding to the uncertainties in the relevant cross sections. Available airglow data give an upper limit of 10 kilorayleighs on the noon zenith intensity due to both mechanisms combined. Other possible sources of excitation are also considered. Recombination of atomic oxygen, the mechanism responsible for the nightglow, does not contribute significantly above 120 km. Fluorescence and collisions with thermal electrons are also negligible, but collisions with energetic photoelectrons may be important.

1. Introduction

The recently developed techniques for measuring the day airglow provide a promising new source of information on conditions in the upper atmosphere and the processes which occur there. Among the more prominent features in the visible portion of the dayglow spectrum are the red and green lines of atomic oxygen. The dayglow red line has been discussed in recent papers by Noxon (1964) and by Dalgarno and Walker (1964). This paper presents a theoretical treatment of the dayglow green line.

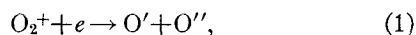
2. Atomic oxygen recombination

The nocturnal green line is believed to result directly from the three-body recombination of oxygen atoms (Chapman, 1931; Dalgarno, 1963; Barth, 1964; Bates, 1964).

Because the recombination rate decreases rapidly with increasing altitude, this mechanism provides a negligible source of $O(^1S)$ atoms above 130 km. In fact, the nightglow measurements show a zenith intensity of less than 20 R at this altitude (see below). The contribution of atomic oxygen recombination to the dayglow is probably comparable. However, the dayglow data (Wallace and Nidey, 1964; Silverman, Lloyd, Cochrun and Nardone, 1964) show zenith intensities of more than 300 R at 130 km, so there must be an additional source of $O(^1S)$ atoms during the day.

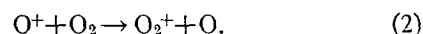
3. Recombination of molecular oxygen ions

3.1. Dependence on ionospheric reaction rates. Nicolet (1954) pointed out that dissociative recombination of O_2^+ ,



is a potential source of green line excitation, and Wallace and Nidey (1964) calculated the contribution of this

mechanism to the dayglow, treating only the recombination of those O_2^+ ions which are produced directly by photoionization. Additional potentially important sources of O_2^+ are provided by the ion-atom interchange reaction,



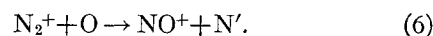
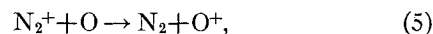
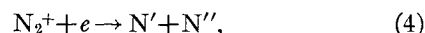
and the charge-exchange reaction,



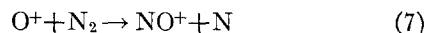
In order to calculate the rate of the O_2^+ recombination reaction (1) in the ionosphere, we follow Norton, Van Zandt and Denison (1963), Wallace and Nidey (1964), Dalgarno and Walker (1964), Whitten and Poppoff (1964), and Zipf and Fastie (1964) in assuming that local equilibrium prevails between ion production and removal rates.

Dalgarno and McElroy (1965) have calculated the rates of production of ions by the direct action of solar ultraviolet radiation, $q(O^+)$, $q(N_2^+)$, and $q(O_2^+)$ $\text{cm}^{-3} \text{sec}^{-1}$, for a wide range of atmospheric models and solar zenith angles. In order to estimate what fractions of the ions, N_2^+ and O^+ , are converted to O_2^+ ions, it is necessary to consider the reactions which remove these ions (cf. Nicolet and Swider, 1963; Dalgarno, 1964). These reactions are indicated in Fig. 1.

In addition to (3), N_2^+ is removed by



The O^+ ions are removed by the ion-atom interchange reactions, (2) and



(Bates, 1955). We follow Dalgarno and Walker (1964) in using for the rate coefficients of these reactions

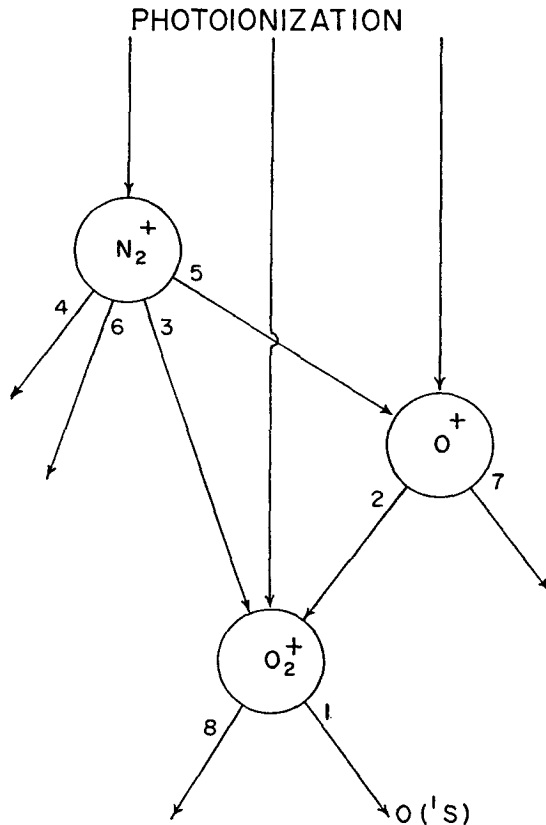
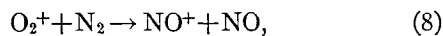


FIG. 1. Ionospheric chemistry contributing to the production of $O(^1S)$. The numbers identify the reactions presented in the text.

$\alpha_1 = 1 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$, $\alpha_2 = \alpha_5 = \alpha_6 = \alpha_7 = 1 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$, $\alpha_3 = 2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$, and $\alpha_4 = 2 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ (Fite, Rutherford, Snow and van Lint, 1962; Biondi, 1964; Norton, Van Zandt and Denison, 1963; Whitten and Poppoff, 1964; Zipf and Fastie, 1964; Sayers and Smith, 1964; Fehsenfeld, Schmeltekopf and Ferguson, 1965a, 1965b), where α_i is the rate coefficient of reaction (i).

Over most of the altitude region of present interest, O_2^+ ions are removed by dissociative recombination, (1). However, at low altitudes the reaction,



may be important (cf. Nicolet and Swider, 1963). We use $\alpha_8 = 1 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$, consistent with the upper limit imposed by the laboratory measurements of Galli, Giordini-Guidoni and Volpi (1963).

If f is the probability that (1) produces an $O(^1S)$ atom, the rate of production is given by

$$Q = f \left\{ q(O_2^+) + q(N_2^+) \left[\frac{\alpha_3 n(O_2) + \frac{\alpha_5 n(O)}{1 + \frac{\alpha_7 n(N_2)}{\alpha_3 n(O_2)}}}{\alpha_3 n(O_2)} \right] \right.$$

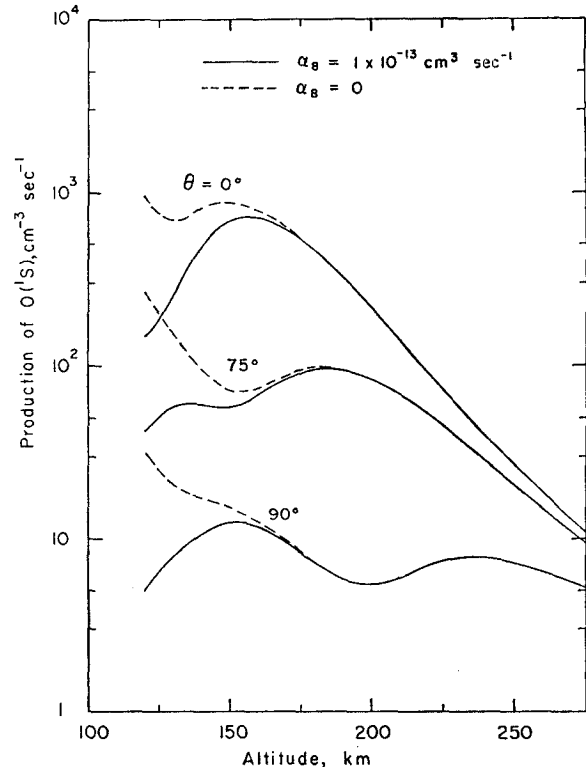


FIG. 2. Dependence on altitude of the rate of production of $O(^1S)$ atoms by O_2^+ recombination for the low O_2 atmosphere. Results are shown for several values of solar zenith angle, θ , and correspond to $\alpha_3/\alpha_4 = 10^{-3}$, $\alpha_5/\alpha_4 = \alpha_6/\alpha_4 = 5 \times 10^{-5}$, $\alpha_2/\alpha_7 = 1$, $\alpha_1 = 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$, and $f = 1$.

$$\times [\alpha_4 n(e) + \alpha_3 n(O_2) + (\alpha_5 + \alpha_6) n(O)]^{-1} + q(O^+) \left[1 + \frac{\alpha_7 n(N_2)}{\alpha_2 n(O_2)} \right]^{-1} \left\{ 1 + \frac{\alpha_3 n(N_2)}{\alpha_1 n(e)} \right\}^{-1}. \quad (9)$$

In evaluating Q we have used two of the model atmospheres considered by Dalgarno and Walker (1964) in their study of the red line. These two models reflect the range of possible values for the composition of the upper atmosphere. The low O_2 atmosphere has number densities at 120 km given by $n(O_2) = 2 \times 10^{10} \text{ cm}^{-3}$, $n(O) = 2 \times 10^{11} \text{ cm}^{-3}$, and $n(N_2) = 5 \times 10^{11} \text{ cm}^{-3}$, while the high O_2 atmosphere contains five times as much O_2 and one fourth as much O . The exospheric temperatures, 750K for the low O_2 atmosphere and 1000K for the high O_2 atmosphere, are chosen so that both models closely reproduce the daytime satellite drag densities measured during 1962. The electron densities, $n(e)$, are taken from the direct measurements of Brace, Spencer and Carignan (1963) on NASA Flight 6.04.

For the low O_2 atmosphere, Q is shown in Fig. 2 as a function of altitude for several solar zenith angles. These results correspond to $f = 1$, so they provide an upper limit on the possible excitation rates consistent

with the adopted ultraviolet flux, model atmosphere, and reaction rate coefficients. In order to illustrate the extent to which the results depend on the value of α_3 , Fig. 2 compares the results of calculations with $\alpha_3=0$ and $\alpha_3=1\times 10^{-13}$ cm³ sec⁻¹. For the high O₂ atmosphere, the fractional change in Q produced by this change in α_3 is practically the same.

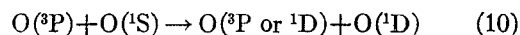
Because (2) is not an important source of O₂⁺ at low altitudes where the ion production rates are large, the green line intensity is not sensitive to the values of α_2 and α_7 . On the other hand, (3) is an important source of O₂⁺ if α_3 is as large as 10^{-10} cm³ sec⁻¹, so the results are sensitive to the relative rates of the reactions, (3), (4), (5), and (6), which remove N₂⁺. A high estimate of Q is obtained by replacing $\alpha_5=\alpha_6=1\times 10^{-11}$ cm³ sec⁻¹ by $\alpha_5=\alpha_6=0$, and a low estimate is obtained by replacing $\alpha_3=2\times 10^{-10}$ cm³ sec⁻¹ by $\alpha_3=0$. The corresponding range in the values of Q is shown in Fig. 3 for the low O₂ atmosphere.

That Q is markedly sensitive to the O₂ concentration is seen by comparing Fig. 3 with Fig. 4, which shows the corresponding values of Q for the high O₂ atmosphere.

3.2. Deactivation of O(¹S). The radiative lifetime of O(¹S) is 0.74 second (Garstang, 1951; cf. Nicholls, 1964), which is much shorter than the lifetime for deactivation in collisions with N₂, O₂, or electrons at altitudes above 100 km. The deactivation rate coefficients

are $<10^{-16}$ cm³ sec⁻¹ for collisions with N₂ (Noxon, 1962; Young and Sharpless, 1963), $\sim 4\times 10^{-15}$ cm³ sec⁻¹ for collisions with O₂ (Kvifte and Vegard, 1947; Barth and Hildebrandt, 1961), and $\sim 2\times 10^{-9}$ cm³ sec⁻¹ for collisions with electrons (Seaton, 1956).

There is no quantitative information on deactivation in collisions with O,



(Young and Sharpless, 1963; cf. Bates, 1964). In order to be important above 120 km, (10) would need a rate coefficient of at least 3×10^{-12} cm³ sec⁻¹ which seems unlikely.

Observations of auroral time variations (Omholt, 1959) and of decay of $\lambda 5577$ in meteor trains (Halliday, 1960) show no evidence of strong deactivation at altitudes as low as 80 km, in agreement with these considerations. Accordingly, collisional deactivation of O(¹S) is ignored at altitudes above 120 km.

During the day there exists the possibility that O(¹S) may be removed by the resonant absorption of solar radiation, a mechanism considered by Dalgarno and Walker (1964) for deactivation of O(¹D).

If the incident solar flux, F_λ cm⁻² sec⁻¹ Å⁻¹, is assumed constant over the width of the absorption line, the probability that an atom in state β will be excited to

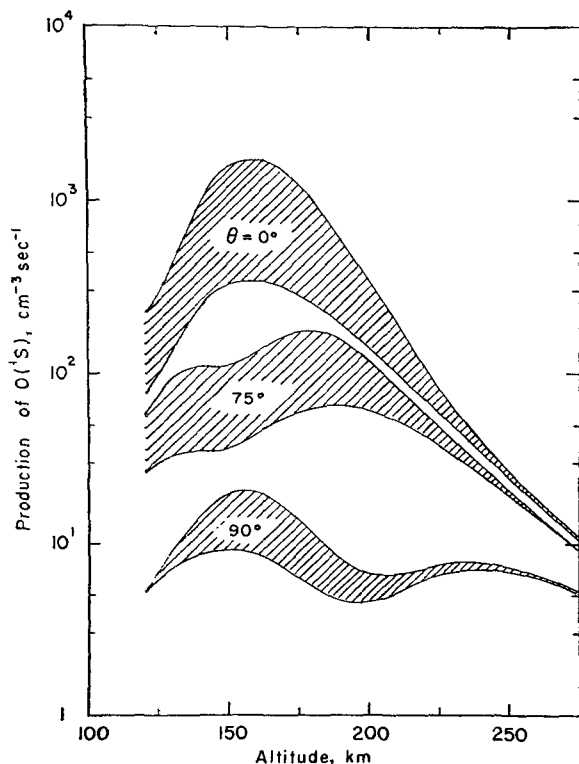


FIG. 3. Range in the values of the O(¹S) production rate which results when the fraction of the N₂⁺ ions converted into O₂⁺ ions is varied between permissible limits. The results correspond to the low O₂ atmosphere.

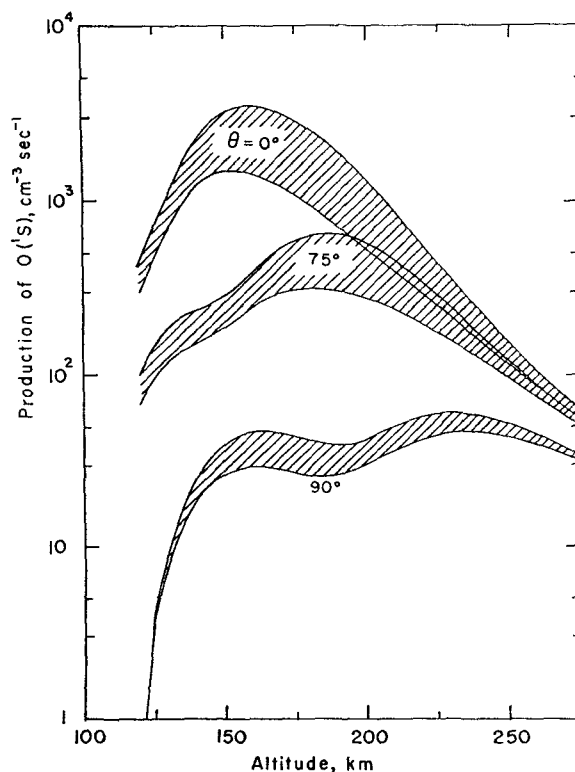


FIG. 4. Range in the values of the O(¹S) production rate which results when the fraction of the N₂⁺ ions converted into O₂⁺ ions is varied between permissible limits. The results correspond to the high O₂ atmosphere.

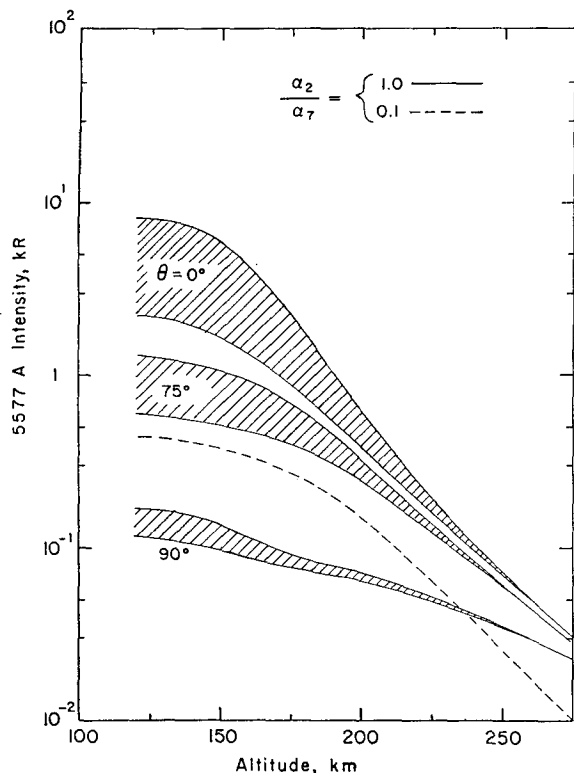


FIG. 5. Dependence on altitude of the green line zenith intensity due to O_2^+ recombination in the low O_2 atmosphere. The upper limits of the cross-hatched areas correspond to values for the rate coefficients which maximize the conversion of N_2^+ into O_2^+ while the lower limits correspond to values which minimize this conversion. The broken line at $\theta = 75^\circ$ shows the further decrease in intensity which results from a reduction in the fraction of the O^+ ions converted to O_2^+ ions.

state α is given by

$$P = \frac{\pi e^2}{mc} f_{\beta\alpha} F_\lambda \frac{\lambda^2}{c(10)^8} \text{ sec}^{-1}, \quad (11)$$

where $f_{\beta\alpha}$ is the oscillator strength of the β to α transition at wavelength λ Å, and e , m , and c are the electronic charge and mass and the velocity of light (cf. Chamberlain, 1961, p. 18). In the wavelength region of interest for the deactivation of $O(^1S)$, $\lambda < 1218$ Å, the peak value of F_λ occurs in the Lyman α line of hydrogen, where $F_\lambda \sim 3 \times 10^{11} \text{ cm}^{-2} \text{ sec}^{-1} \text{ Å}^{-1}$ (cf. Tousey, 1963). The strongest absorption by $O(^1S)$ occurs in the transition to the $^1P^\circ$ term. The corresponding oscillator strength is 0.176 (Kelly, 1964; Allen, 1963), so that the probability of resonance deactivation of $O(^1S)$ is less than $7 \times 10^{-4} \text{ sec}^{-1}$. This is negligible compared with the probability of emission of $\lambda 5577$.

It is therefore assumed that $O(^1S)$ does not suffer deactivation at altitudes above 120 km. Of the $O(^1S)$ atoms formed at these altitudes, 94 per cent (Garstang, 1951; cf. Nicholls, 1964) are removed by

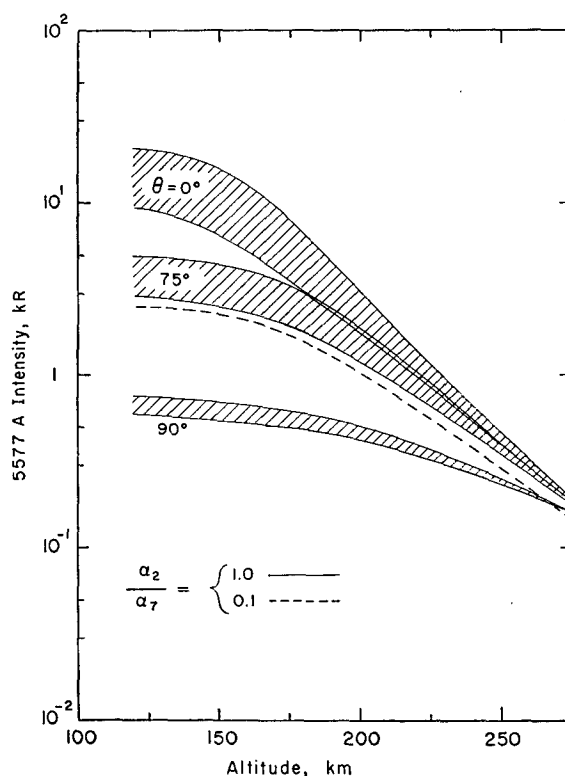
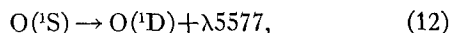
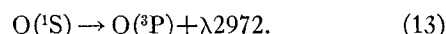


FIG. 6. Dependence on altitude of the green line zenith intensity due to O_2^+ recombination in the high O_2 atmosphere. The upper limits of the cross-hatched areas correspond to values for the rate coefficients which maximize the conversion of N_2^+ into O_2^+ while the lower limits correspond to values which minimize this conversion. The broken line at $\theta = 75^\circ$ shows the further decrease in intensity which results from a reduction in the fraction of the O^+ ions converted to O_2^+ ions.

and the remaining 6 per cent by



The emission rates are therefore directly proportional to the $O(^1S)$ production rates shown in Figs. 2, 3 and 4. Figs. 5 and 6 show the range in the green line zenith intensity as a function of altitude corresponding to the range in the production rates shown in Figs. 3 and 4.

In order to indicate the extent to which the results depend on the value of α_2/α_7 , the broken curves in Figs. 5 and 6 show the intensity at a solar zenith angle of 75° which results when $\alpha_2/\alpha_7 = 0.1$ is used in the calculations. The broken curves should be compared with the curves forming the lower limits of the $\theta = 75^\circ$ cross-hatched areas, which correspond to $\alpha_2/\alpha_7 = 1.0$ but are identical in all other parameters.

3.3. Yield of $O(^1S)$ atoms. Fig. 7 shows the green line zenith intensity at 120 km as a function of solar zenith angle for both model atmospheres. The cross-hatched areas correspond to the choice of rate coefficients which led to the cross-hatched areas in Figs. 3, 4, 5 and 6. Also shown is an upper limit on the green line zenith intensity established by Noxon (1963) in an observation at Fort

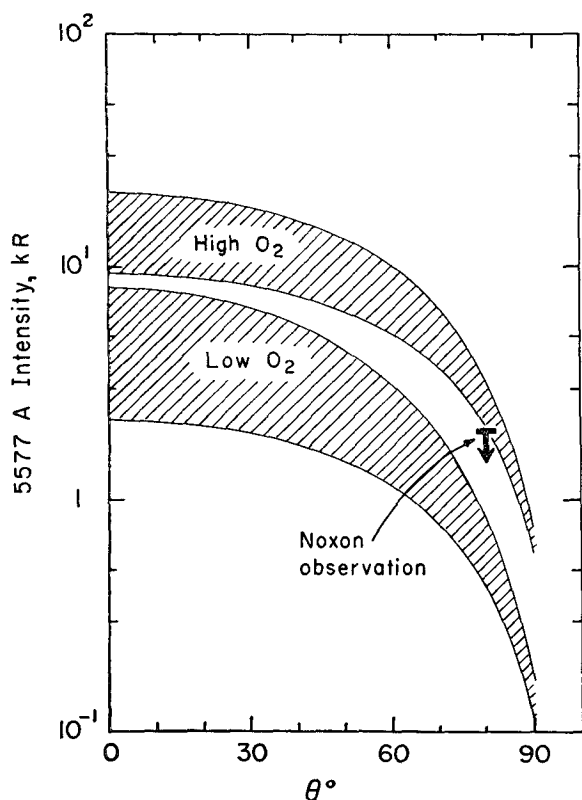


FIG. 7. Dependence on solar zenith angle of the intensity at 120 km which results from O_2^+ recombination. The cross-hatched areas correspond to the uncertainty in the conversion of N_2^+ into O_2^+ .

Churchill in December 1962. The high O_2 atmosphere predicts excessive intensities and, in order to be consistent with Noxon's observation, the yield, f , of $O(^1S)$ atoms in O_2^+ recombination must be less than 1. The variation of the intensity with solar zenith angle is such that the noon value can be no greater than 10 kR if O_2^+ recombination is the principal source of the dayglow green line.

It is possible that independent information on the value of f might be provided by rocket measurements of the nightglow. Measurements of the nocturnal $\lambda 5577$ intensity as a function of altitude have been made by Berg, Koomen, Meredith and Scolnik (1956), Koomen, Scolnik and Tousey (1956), Heppner and Meredith (1958), Tarasova (1963), and O'Brien, Allum and Goldwire (1965). The earlier results have been reviewed by Tousey (1958) and by Packer (1961). None of these experiments have detected green line emission above 130 km, and this probably implies an upper limit of 20 R on the zenith intensity at this altitude. Coupled with information on the integrated O_2^+ recombination rate in the nocturnal ionosphere this figure can be used to set an upper limit on f .

Assuming that dissociative recombination of O_2^+ (1) is the predominant source of $\lambda 6300$ at night (cf. Chamberlain, 1961; Dalgarno and Walker, 1964), we can use

data on the nightglow red line to obtain information on the integrated O_2^+ recombination rate.

On a rocket flight which detected less than 20 R of $\lambda 5577$ at 130 km, Tarasova (1963) measured a red line zenith intensity of 170 R at this height. This implies that $f(^1S)/f(^1D) < 0.12$, where $f(X)$ is the probability that (1) yields an oxygen atom in term X , and collisional deactivation of $O(^1D)$ is allowed for by the inequality. The maximum possible value of $f(^1D)$ is 2. Accordingly, $f(^1S) < 0.24$, provided that O_2^+ recombination is the only important source of $\lambda 6300$ at night. From Fig. 7 there follows a corresponding upper limit of 5 kR on the contribution of dissociative recombination to the green line zenith intensity at noon.

Alternatively, the argument might be based on observed profiles of ion and electron density rather than on nightglow red line data. Fig. 8 shows the product of the electron concentration and the O_2^+ concentration measured by Holmes, Johnson and Young (1965) on two rocket flights at White Sands in 1963. This product would be proportional to the $O(^1S)$ production rate if the recombination rate coefficient were independent of altitude.

The daytime curve in Fig. 8 has about the same shape as the theoretical curves in Figs. 3 and 4 and yields a green line zenith intensity of 4 kR if $f(^1S)=1$ and $\alpha_1=10^{-7} \text{ cm}^3 \text{ sec}^{-1}$, independent of altitude. This value is consistent with Noxon's limit and lies between the results for the high O_2 and low O_2 atmospheres shown in Fig. 7.

The corresponding contribution to the nightglow from the altitude region below 230 km for which ion density data are available is only 2 R, which is consistent with the nightglow observations. However, it is clear from Fig. 8 that the nocturnal recombination of O_2^+ is peaked above 230 km. Accordingly, it is possible that useful deductions could be made if ion and electron density data were available at higher altitudes. At present we can only conclude that $f=1$ does not contradict the ion density data.

4. Electron impact

It appears that electron impact excitation may contribute significantly to the oxygen red line in the dayglow (Noxon, 1964; Dalgarno and Walker, 1964). The green line excitation due to thermal electrons (the electrons having a Maxwell-Boltzmann energy distribution corresponding to an electron temperature which may differ from the neutral gas temperature) may readily be calculated using rate coefficients derived from Seaton (1956). On account of the relatively large excitation energy of $O(^1S)$, thermal electron excitation would contribute only 70 R to the green line zenith intensity even if the electron temperature were as high as 4000K at all altitudes. The contribution will be negligible for the lower electron temperatures normally measured in the ionosphere (Brace, Spencer and Carignan, 1963; Bowen, Boyd, Henderson and Will-

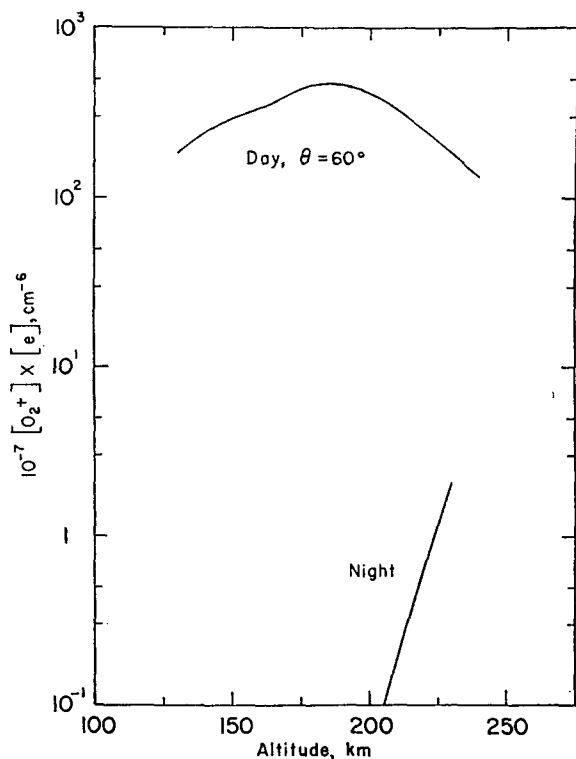


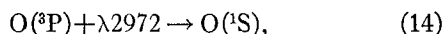
FIG. 8. The product of the O_2^+ and electron densities measured by Holmes, Johnson and Young (1965). This product would be proportional to the $O(^1S)$ production rate if the O_2^+ recombination rate coefficient were independent of altitude.

more, 1964; Brace, Spencer and Dalgarno, 1965; Spencer, Brace, Carignan, Taesch and Niemann, 1965).

Excitation caused by collisions with non-thermal photoelectrons is being evaluated by other workers (M. B. McElroy, private communication, 1965). This contribution appears to be large.

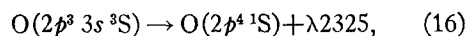
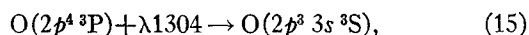
5. Fluorescent excitation

Production of $O(^1S)$ atoms by the direct absorption of solar radiation,



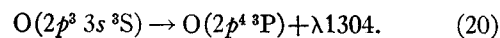
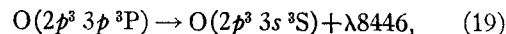
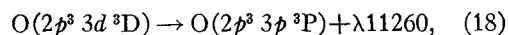
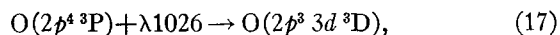
has been discussed by Bates and Massey (1946), Bates and Dalgarno (1954), and Chamberlain (1961, p. 425). The contribution of this process to the green line zenith intensity in the dayglow is only about 20 R.

Fluorescence through the sequence,



has been considered by Dalgarno and Walker (1964). Their argument indicates that (15) and (16) contribute less than 1 R to the green line zenith intensity.

Brandt (1959) has considered fluorescence by oxygen atoms in the sequence,



The possible importance of transitions from any of the excited states, 3D , 3P , or 3S , to $O(2p^4\ ^1S)$ should be considered. However, since the probability of such forbidden transitions is $\lesssim 10^{-5}$, and since Brandt estimates a zenith intensity at $\lambda 8446$ of only 500 R, the contribution to the green line intensity (and also to the red line intensity) is negligible. [Brandt's estimate of the intensity of $\lambda 8446$ was based on an early measurement of the solar Lyman β flux at $1026\ \text{\AA}$ which now appears to have been too large by an order of magnitude (cf. Tousey, 1963).]

6. Photodissociation of molecular oxygen

Bates and Dalgarno (1954) called attention to the possible importance of photodissociation of O_2 at wavelengths shorter than $1335\ \text{\AA}$ as a source of $O(^1S)$ atoms, estimating that the resulting zenith intensity might be as high as 10 kR. Because the absorption processes of O_2 in this spectral region have not been identified, the yield of $O(^1S)$ atoms is not known.

In discussing this mechanism, we will concentrate on the five dominant features in the $1050\ \text{\AA}$ to $1335\ \text{\AA}$ region for which absorption coefficients have recently been published by Metzger and Cook (1964). The cross sections are given in Table 1 together with approximate values of the solar flux integrated over each absorption maximum (Hinteregger, 1961; Hinteregger and Watanabe, 1962; Tousey, 1963).

Assuming that each absorption yields one excited atom and that deactivation is negligible, the zenith intensity is given approximately by

$$I(\theta) = 0.94F \cos\theta, \quad (21)$$

where θ is the solar zenith angle, F is the incident solar flux, and it is assumed that the atmosphere is optically thick to the absorbed radiation. This expression is valid for $\theta \lesssim 85^\circ$.

Using the solar fluxes of Table 1 in (21) we see that the contribution to the green line intensity would be significant if absorption in any of these maxima were to yield $O(^1S)$ atoms.

If it is assumed, consistent with Noxon's (1963)

TABLE 1. Absorption maxima of O_2 .

Wavelength of maximum absorption \AA	Absorption cross section cm^2	Solar flux $\text{cm}^{-2}\ \text{sec}^{-1}$
1153	$7.44(-18)^*$	2(9)
1205	$1.60(-17)$	5(9)
1244	$4.46(-17)$	2(9)
1292	$7.44(-19)$	3(9)
1333	$2.05(-18)$	2(10)

* $7.44(-18) = 7.44 \times 10^{-18}$.

observation, that photodissociation contributes no more than 2 kR to the zenith intensity at $\theta=80^\circ$, then (21) gives

$$I(\theta) < 10 \cos \theta \text{ kR}, \quad \theta \leq 80^\circ. \quad (22)$$

The inequality allows for the possible effects of collisional deactivation at low altitudes as well as the spherical geometry of the atmosphere. In comparing this observational limit with the intensities predicted by (21) and the solar fluxes in Table 1, it appears that not all of these absorption maxima can yield $O(^1S)$ atoms. Since the absorption maxima in Table 1 represent only a small part of the O_2 absorption spectrum in the 1030 Å to 1335 Å region, it follows that only a small fraction of the absorptions in this spectral region yield $O(^1S)$ atoms.

An upper limit on the possible contribution of photodissociation to the intensity as a function of altitude is obtained by considering only the strongest absorption maximum at 1244 Å and choosing the solar flux to give 2 kR of green line at $\theta=80^\circ$. The resulting zenith intensity as a function of altitude is shown in Fig. 9 for both model atmospheres, assumed to be spherically symmetric, and several values of the solar zenith angle. The corresponding solar fluxes are about $10^{10} \text{ cm}^{-2} \text{ sec}^{-1}$. The effect on the theoretical altitude profiles of decreasing either the cross section, σ , or the solar flux, F , is indicated, schematically, in Fig. 10.

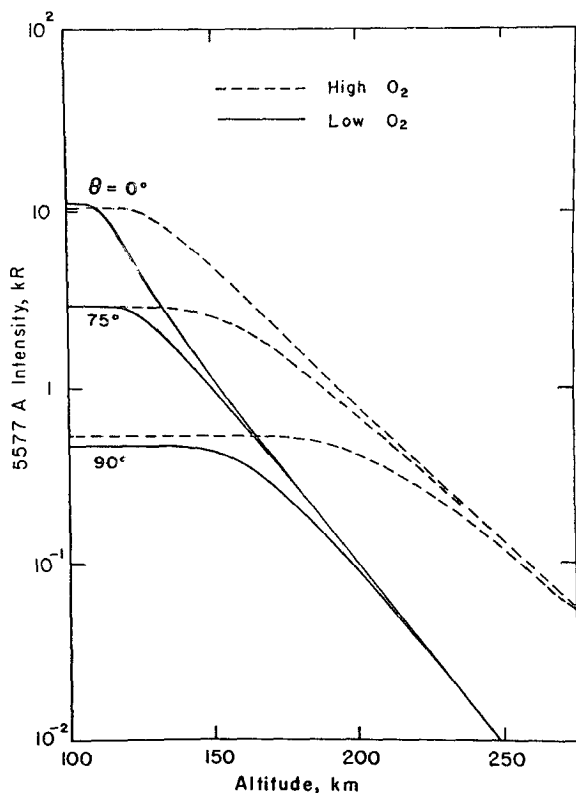


FIG. 9. Upper limits on the zenith intensity as a function of altitude which results from photodissociation of O_2 . The calculations assume spherically symmetric atmospheres.

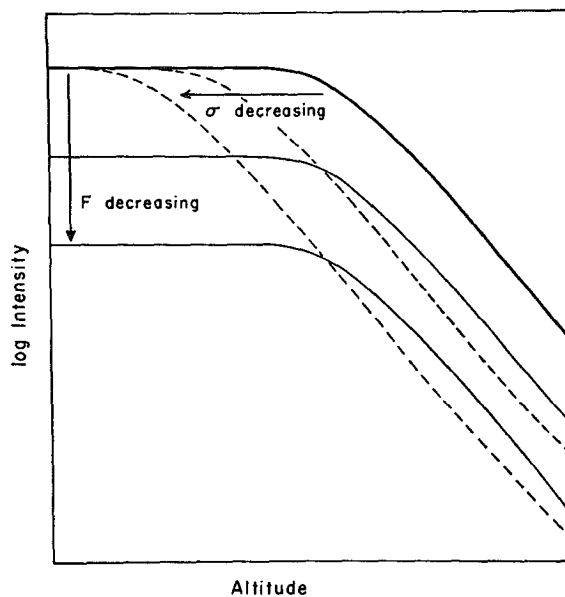


FIG. 10. Possible altitude profiles of the intensity due to photodissociation. The heavy line represents the upper limit. The light lines show the profiles for smaller dissociating fluxes while the broken lines show the profiles for smaller effective absorption cross sections.

The upper limits on the zenith intensities at a solar zenith angle of 95° are 120 R and 75 R for the high O_2 and low O_2 atmospheres, respectively. At 100° the corresponding values are 8 R and 2 R. Photodissociation of O_2 cannot, therefore, contribute to the observed, variable, twilight enhancement of the green line (Dufay and Dufay, 1948; Megill, 1960).

The nocturnal flux of Lyman α radiation is $10^{-2} \text{ erg cm}^{-2} \text{ sec}^{-1}$ (Kupperian, Byram, Chubb and Friedman, 1959) or $6 \times 10^8 \text{ photons cm}^{-2} \text{ sec}^{-1}$. If a substantial fraction of these photons were to photodissociate O_2 and produce $O(^1S)$ atoms in the process, the contribution to the nightglow green line would be significant. However, an upper limit of 15 R on this contribution follows from Noxon's dayglow observation and the daytime Lyman α flux of $6 \text{ erg cm}^{-2} \text{ sec}^{-1}$ (cf. Tousey, 1963).

7. Conclusion

Both photodissociation of molecular oxygen and dissociative recombination of O_2^+ could contribute significantly to the $\lambda 5577$ dayglow. A limit of 10 kR at noon on the zenith intensity due to both mechanisms together is provided by Noxon's observation that the intensity is less than 2 kR at a solar zenith angle of 80° . From the limit on the photodissociation source it follows that few absorptions by O_2 of radiation in the 1030 Å to 1335 Å region yield $O(^1S)$ atoms.

Rocket measurements of the nocturnal red and green lines suggest that dissociative recombination of O_2^+ yields fewer than 0.24 $O(^1S)$ atoms per recombination. This leads to an upper limit of 5 kR on the dissociative

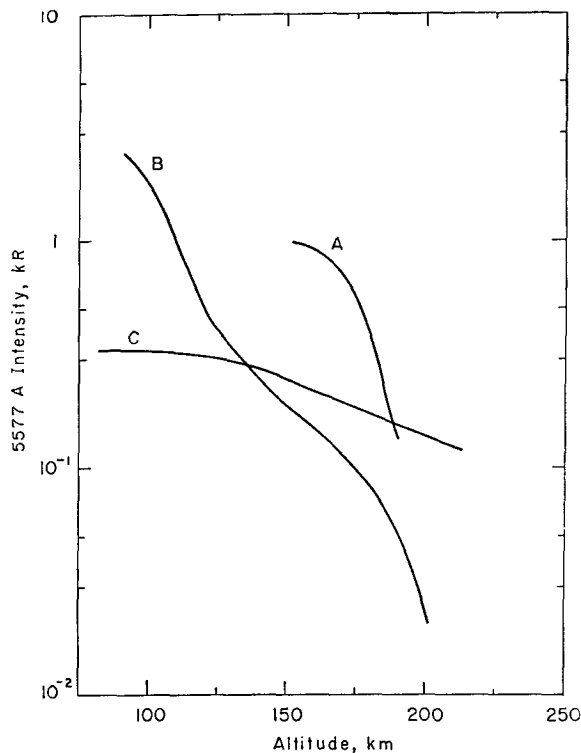


FIG. 11. Measured altitude profiles of the green line intensity (Wallace and Nidey, 1964; Silverman, Lloyd, Cochran and Nardone, 1964). A—Wallace, White Sands, 6:20 a.m., 25 June 1963, B—Silverman, Fort Churchill, 6:22 a.m., 18 July 1964, C—Silverman, White Sands, 4:00 p.m., 13 November 1963.

recombination contribution to the green line zenith intensity at noon.

The available measurements of the dayglow green line (Wallace and Nidey, 1964; Silverman, Lloyd, Cochran and Nardone, 1964) are compared in Fig. 11. While curve B can probably be disregarded as it is believed to reflect the presence of an aurora, the difference between curves A and C is too great to be explained in terms of the excitation sources discussed in this paper. It is therefore felt that detailed interpretation can most profitably be undertaken when additional data on the altitude dependence of the green line intensity are available.

Acknowledgments. I am grateful to Dr. A. Dalgarno for his advice and encouragement, and to Dr. J. F. Noxon, Dr. S. M. Silverman, and Mr. J. W. F. Lloyd for the benefit of helpful discussions. A number of useful suggestions were made by Drs. D. M. Hunten and M. B. McElroy. Mrs. O. P. Ko provided valuable assistance in programming and running the computer.

A part of this research was performed while I was at Columbia University, and was supported by the National Aeronautics and Space Administration under Grant Number NsG-445. A National Academy of Sciences-National Research Council Research Associateship has enabled me to continue this work.

REFERENCES

- Allen, C. W., 1963: *Astrophysical Quantities*. University of London Press, London.
- Barth, C. A., 1964: Three body reactions. *Ann. Geophys.*, **20**, 182-196.
- , and A. F. Hildebrandt, 1961: The 5577 Å airglow emission mechanism. *J. Geophys. Res.*, **66**, 985-986.
- Bates, D. R., 1955: Charge transfer and ion-atom interchange collisions. *Proc. Phys. Soc. London*, **A68**, 344-345.
- , 1964: Chemical reactions contributing to the nightglow. *Discussions Faraday Soc.*, **37**, 21-25.
- , and A. Dalgarno, 1954: Theoretical considerations regarding the dayglow. *J. Atmos. Terr. Phys.*, **5**, 329-344.
- , and H. S. W. Massey, 1946: The basic reactions in the upper atmosphere. I. *Proc. Roy. Soc. London*, **A187**, 261-296.
- Berg, O. E., M. Koomen, L. Meredith and R. Scolnik, 1956: The altitude of the (OI) 5577 Å line in the night airglow measured from a rocket. *J. Geophys. Res.*, **61**, 302-303.
- Biondi, M. A., 1964: Electron-ion and ion-ion recombination. *Ann. Geophys.*, **20**, 34-46.
- Bowen, P. J., R. L. F. Boyd, C. L. Henderson and A. P. Willmore, 1964: Electron temperature in the upper F-region. *Proc. Roy. Soc. London*, **A281**, 526-538.
- Brace, L. H., N. W. Spencer and G. R. Carignan, 1963: Ionosphere electron temperature measurements and their implications. *J. Geophys. Res.*, **68**, 5397-5412.
- , —, and A. Dalgarno, 1965: Detailed behavior of the mid-latitude ionosphere from the Explorer XVII satellite. *Planetary Space Sci.*, in press.
- Brandt, J. C., 1959: Solar Lyman-β fluorescence mechanism in the upper atmosphere. *Astrophys. J.*, **130**, 228-240.
- Chamberlain, J. W., 1961: *Physics of the Aurora and Airglow*. New York, Academic Press, 704 pp.
- Chapman, S., 1931: Some phenomena of the upper atmosphere (Bakerian Lecture). *Proc. Roy. Soc. London*, **A132**, 353-374.
- Dalgarno, A., 1963: Vibrationally excited molecules in atmospheric reactions. *Planetary Space Sci.*, **10**, 19-28.
- , 1964: Thermal reactions involving charged particles. *Discussions Faraday Soc.*, **37**, 142-148.
- , and M. B. McElroy, 1965: Electron and ion production rates in the upper atmosphere. To be published.
- , and J. C. G. Walker, 1964: The red line of atomic oxygen in the day airglow. *J. Atmos. Sci.*, **21**, 463-474.
- Dufay, J., and M. Dufay, 1948: Excitation de la raie verte de l'oxygène au crépuscule. *Compt. Rend.*, **226**, 1208-1210.
- Fehsenfeld, F. C., A. L. Schmeltekopf and E. E. Ferguson, 1965a: Some measured rates for oxygen and nitrogen ion-molecule reactions of atmospheric importance, including $O^+ + N_2 \rightarrow NO^+ + N$. *Planetary Space Sci.*, in press.
- , —, and —, 1965b: Correction in the laboratory measurement of the rate constant for $N_2^+ + O_2 \rightarrow N_2 + O_2^+$ at 300°K. *Planetary Space Sci.*, in press.
- Fite, W. L., J. A. Rutherford, W. R. Snow and V. A. J. van Lint, 1962: Ion-neutral collisions in afterglow. *Discussions Faraday Soc.*, **33**, 264-272.
- Galli, A., A. Giordini-Guidoni and G. G. Volpi, 1963: Ion-molecule reactions leading to NO^+ formation. *J. Chem. Phys.*, **39**, 518-521.
- Garstang, R. H., 1951: Energy levels and transition probabilities in p^2 and p^4 configurations. *Monthly Notices Roy. Astron. Soc.*, **111**, 115-124.
- Halliday, I., 1960: Auroral green line in meteor wakes. *Astrophys. J.*, **131**, 25-33.
- Heppner, J. P., and L. H. Meredith, 1958: Nightglow emission altitudes from rocket measurements. *J. Geophys. Res.*, **63**, 51-65.
- Hinteregger, H. E., 1961: Preliminary data on solar extreme ultraviolet radiation in the upper atmosphere. *J. Geophys. Res.*, **66**, 2367-2380.

- , and K. Watanabe, 1962: Photoionization rates in the *E* and *F* regions, 2. *J. Geophys. Res.*, **67**, 3373–3392.
- Holmes, J. C., C. Y. Johnson and J. M. Young, 1965: Ionospheric chemistry. *Space Research*, **5**, Amsterdam, North-Holland Publishing Company, pp. 756–766.
- Kelly, P. S., 1964: Transition probabilities in nitrogen and oxygen from Hartree-Fock-Slater wave functions. *J. Quant. Spectrosc. Radiat. Transfer*, **4**, 117–148.
- Koomen, M., R. Scolnik and R. Tousey, 1956: Distribution of the night airglow (OI) 5577 Å and Na *D* layers measured from a rocket. *J. Geophys. Res.*, **61**, 304–306.
- Kupperian, J. E., E. T. Byram, T. A. Chubb and H. Friedman, 1959: Far ultraviolet radiation in the night sky. *Planetary Space Sci.*, **1**, 3–6.
- Kvifte, G., and L. Vegard, 1947: On the emission of the forbidden lines from the metastable groundstates 1S_0 and 1D_2 of the neutral oxygen atom. *Geophys. Publik.*, **17**, No. 1, 1–34.
- Megill, L. R., 1960: Photometric observations of the twilight glow [OI] 5577 and [OI] 6300. *J. Atmos. Terr. Phys.*, **17**, 276–285.
- Metzger, P. H., and G. R. Cook, 1964: A reinvestigation of the absorption cross sections of molecular oxygen in the 1050–1800 Å region. *J. Quant. Spectrosc. Radiat. Transfer*, **4**, 107–116.
- Nicholls, R. W., 1964: Transition probabilities of aeronomically important spectra. *Ann. Geophys.*, **20**, 144–181.
- Nicolet, M., 1954: Origin of the emission of the oxygen green line in the airglow. *Phys. Rev.*, **93**, 633.
- , and W. Swider, 1963: Ionospheric conditions. *Planetary Space Sci.*, **11**, 1459–1482.
- Norton, R. B., T. E. Van Zandt and J. S. Denison, 1963: A model of the atmosphere and ionosphere in the *E* and *F1* regions. *Proceedings International Conference on the Ionosphere*, London, Institute of Physics and Physical Society, pp. 26–34.
- Noxon, J. F., 1962: Active nitrogen at high pressure. *J. Chem. Phys.*, **36**, 926–940.
- , 1963: Observation of daytime aurora. *J. Atmos. Terr. Phys.*, **25**, 637–645.
- , 1964: A study of the 6300 Å oxygen line in the day airglow. *J. Geophys. Res.*, **69**, 3245–3255.
- O'Brien, B. J., F. R. Allum and H. C. Goldwire, 1965: Rocket measurement of midlatitude airglow and particle precipitation. *J. Geophys. Res.*, **70**, 161–175.
- Omholt, A., 1959: Studies on the excitation of aurora borealis. II. The forbidden oxygen lines. *Geophys. Publik.*, **21**, No. 1, 1–38.
- Packer, D. M., 1961: Altitudes of the night airglow radiations. *Ann. Geophys.*, **17**, 67–74.
- Sayers, J., and D. Smith, 1964: Ion and charge exchange reactions involving atmospheric gases. *Discussions Faraday Soc.*, **37**, 167–175.
- Seaton, M. J., 1956: The calculation of cross sections for excitation of forbidden atomic lines by electron impact. *The Airglow and the Aurorae*, London, Pergamon Press, pp. 289–301.
- Silverman, S. M., J. W. F. Lloyd, B. L. Cochrun and L. J. Nardone, 1964: Rocket optical observation of a daytime aurora. *Nature*, **204**, 461–462.
- Spencer, N. W., L. H. Brace, G. R. Carignan, D. R. Taesch and H. Niemann, 1965: Electron and molecular nitrogen temperature and density in the thermosphere. *J. Geophys. Res.*, **70**, 2665–2698.
- Tarasova, T. M., 1963: Night-sky emission-line intensity distribution with respect to height. *Space Research*, **3**, Amsterdam, North-Holland Publishing Company, pp. 162–172.
- Tousey, R., 1958: Rocket measurements of the night airglow. *Ann. Geophys.*, **14**, 186–195.
- , 1963: The extreme ultraviolet spectrum of the sun. *Space Science Reviews*, **2**, 3–69.
- Wallace, L., and R. A. Nidey, 1964: Measurement of the daytime airglow in the visual region. *J. Geophys. Res.*, **69**, 471–479.
- Whitten, R. C., and I. G. Poppoff, 1964: Ion kinetics in the lower ionosphere. *J. Atmos. Sci.*, **21**, 117–133.
- Young, R. A., and R. L. Sharpless, 1963: Chemiluminescent reactions involving atomic oxygen and nitrogen. *J. Chem. Phys.*, **319**, 1071–1102.
- Zipf, E. C., and W. G. Fastie, 1964: An observation of the (0,0) negative band of N_2^+ in the dayglow. *J. Geophys. Res.*, **69**, 2357–2368.